Synthesis and Electrochemical Characterization of Orthorhombic $LiMnO_2$ Material

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Introduction

The layered oxide materials, $LiMO_2$ (M=Co, Ni, Mn…) and the $LiMn_2O_4$ spinel are the most widely studied 4 V cathode materials for lithium secondary batteries with high energy density. The Mn-based materials have attracted wide attention as intercalation cathode materials because of their low cost and nontoxicity. Orthorhombic $LiMnO_2$ (herein referred to as o-$LiMnO_2$) of the ordered rock salt structure described by Johnston and Hoppe et al.[1] has been studied many research groups.[1-9] The low temperature synthesis (170~450^{o}C) first reported by Ohzuku et al. showed a large rechargeable capacity above 190mAh/g.[2] Reimers et al. also reported a new ion exchange method and revealed an irreversible structural change to the spinel phase using in-situ XRD.[3]

Croguennec et al. and other groups[4-7] reported a different synthetic route at mid-range temperatures (600~750^{o}C). They contributed to reveal the capacity loss mechanism and improve the cycleability of the o-$LiMnO_2$ material. However, the results showed a reduced initial discharge capacity (about 130mAh/g) and the elevated temperature performance of o-$LiMnO_2$ has not been reported.

Jang et al. also reported that the o-$LiMnO_2$ material, which was synthesized using LiOH and Mn_3O_4 under a reduced oxygen atmosphere by a high temperature synthetic method (> 900^{o}C).[8-9] The material exhibited an excellent cycleability at room temperature at a current density of 45.9mA/g between 4.4 and 2.0 V. They first reported the high temperature performance at 55^{o}C and observed a nanodomain structure in $LiMnO_2$ using TEM and HREM which was produced by a cycling induced phase transformation. To my regret, the capacity loss of o-$LiMnO_2$ at high temperature was much larger than that during the room temperature test.

From a review of previous studies, we found the following problems : First, the complexity of the synthetic process. For the low temperature synthesis, most cases used an excess amount of lithium salt or lithium/sodium exchange reaction to form the homogeneous $LiMnO_2$ phase. It requires a long reaction time and other reaction steps. Even for the high temperature synthesis, very sensitive synthetic conditions and some treatments to improve the reaction between the starting materials are needed. Second, there is no report showing a good cycle performance of o-$LiMnO_2$ at high temperature. And last, o-$LiMnO_2$, which was synthesized at high temperature, needed enough time to reach the maximum discharge capacity at room temperature. Although it critically depends on current density and the cycle test conditions, this indication is not desirable to use this cathode material for lithium secondary batteries.

In this paper, we report the synthetic method and physicochemical characterizations of o-$LiMnO_2$, which can satisfy the above three aspects at the same time.

Experimental

The o-$LiMnO_2$ material was synthesized using LiOH H_2O and γ-MnOOH. The mixture of LiOH and γ-MnOOH (molar ratio of Li/Mn = 1) was thoroughly ground in an agate. The powder X-ray diffraction (XRD) using Cukα radiation was performed to identify the crystalline phase of the materials. The electrochemical characterizations were performed using CR2032 coin-type cells. The electrolyte used was a 1M $LiPF_6$-EC/ DMC (1:2 by vol.). The charge-discharge current density was 0.4 mA/cm^2 with a cut-off voltage of 2.0 to 4.5V.

Results and Discussion

Orthorhombic $LiMnO_2$ was synthesized using LiOH and γ-MnOOH starting materials. X-ray diffraction revealed that the $LiMnO_2$ compound showed a well-defined orthorhombic phase of a Pmnm space group. The lattice constants of the resulting compound are a =2.806 Å, b=5.751 Å, and c= 4.572 Å. The $LiMnO_2$ delivered 193mAh/g in the first cycle and still delivered 181mAh/g after 50 cycles at room temperature. The well-defined orthorhombic $LiMnO_2$ compound exhibited an excellent cycle performance, and can maintain its original structure upon cycling and suppress transformation to the spinel structure.

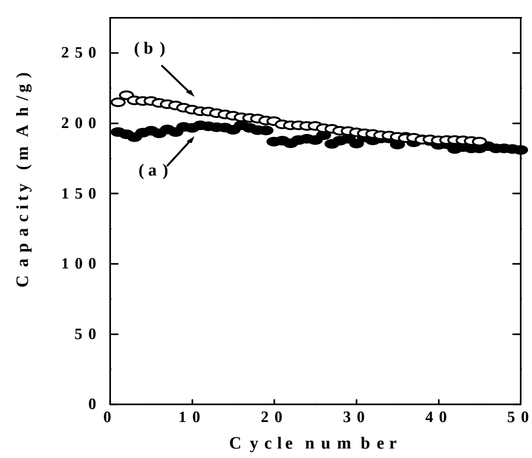

Fig. 1.The plot of specific discharge vs. number of cycle for the Li/1M $LiPF_6$-EC/DMC/$LiMnO_2$ (a) 25^{o}C (b) 50^{o}C.

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